

On Radiation in a Gaseous Explosion.

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In the first report of the British Association Committee on Gaseous Explosions, attention was drawn to the probable importance of radiation in determining the rate of cooling of the mass of hot gas produced by igniting an inflammable mixture in a closed vessel. In the second report reference was made to some experiments which I had made on the effect of coating the walls of the explosion vessel with bright tin-foil. It was found that if a mixture of coal-gas and air of given composition were exploded in a vessel thus lined, the maximum pressure reached was nearly the same as that given by an identical mixture when the tin-foil lining was blackened, but the rate of cooling was decidedly less.

Though the experiment established a substantial difference between the rates of heat-loss in the two cases, it was hardly sufficient to justify giving quantitative results, nor was it absolutely conclusive as to the cause of the difference, though it seemed highly probable that it was due to the difference in the power of the walls to absorb radiant energy.

I have recently completed a more elaborate series of tests, which I think are sufficiently accurate and conclusive for publication. Instead of coating the inside of the vessel with tin-foil, I have had it plated with silver, which has in successive explosions of the same mixture been first highly polished and then blackened. As in the vessel lined with tin-foil, the cooling is slower when the walls are reflecting, but the difference is greater with the silver-lined vessel, amounting to about 50 per cent. during the first quarter of a second. Moreover, there is a difference in maximum pressure, amounting to about 3 per cent. Records have also been obtained of the change of temperature, during the explosion and subsequent cooling, of a bolometer placed outside a window of fluorite in the wall of the vessel, and these have shown that for one-tenth of a second after maximum pressure something like one-third of the whole heat-loss to black walls is due to radiation, and that the radiation is still perceptible half a second after maximum pressure, when the temperature of the gas has fallen to about 1200° C. Of the whole of the heat given up by the gas in cooling from 2100° C. to atmospheric temperature at least one-fifth part goes in radiation.

The explosion vessel employed was cylindrical, the internal dimensions being 30 cm. by 30 cm. It was made of cast iron, and the inner surface

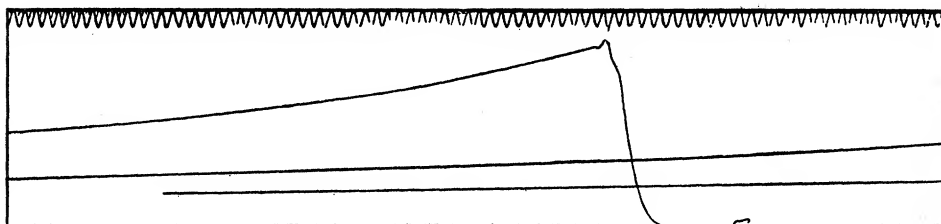
after finishing in the lathe was electro-plated. The polishing was done at first by hand with a leather and rouge, but though this gave a surface which to all appearances was perfectly polished, it was found that appreciably higher pressures and much slower cooling could be obtained by putting more work into the polishing. Accordingly in the later trials a motor-driven buffing wheel was used, and the surface was also carefully washed with alcohol. For blackening the surface, a dead black paint consisting of lamp-black mixed with a little shellac was put on in a thin layer. The weight of this layer when dry was about 1.5 milligramme per square centimetre, and the thickness about 0.02 mm.

The explosive mixture consisted always of 15 parts of Cambridge coal-gas, having a higher calorific value (as determined with a Boys' calorimeter) of about 370 lb.-centigrade thermal units per cubic foot, or say 6000 calories per litre under standard conditions, to 85 of air; this being very nearly the mixture of maximum strength consistent with complete combustion. The mixture was at atmospheric pressure and temperature before firing. The products of combustion contained (by volume) about 8.5 per cent. of CO_2 , and 20 per cent. of H_2O , the remainder being nitrogen with a small amount of excess O. In order to secure strictly comparative results a mixture of gas and air containing about 19 per cent. coal gas was stored in a separate tank for from 3 to 12 hours. A portion of this mixture was then transferred to the partially exhausted explosion vessel, being there diluted with sufficient air to give the required strength of 15 per cent. There was sufficient mixture in the tank to give three or four explosions, and, the quantity of air left in the explosion vessel before admitting the mixture from the tank being only about one-fifth of the whole, small errors in the measurement of this quantity were without appreciable effect upon the strength of mixture, which must have been substantially identical for all charges taken from the same filling of the tank. The first explosion was taken with the vessel highly polished. It was quickly followed with a second explosion of the same mixture, the walls having been in the meantime either repolished or blackened, and a third and sometimes a fourth explosion with blackened walls was taken. In this way three or four explosions were made, one or more of which were with polished walls and the remainder with blackened walls. The conditions for these explosions were identical not only as regards the composition of the charge but also in respect of barometric pressure and temperature.

The pressures were recorded in about 20 cases by a pencil indicator of the outside-spring type made by Dreyer and Company, the ordinary reciprocating drum of which was replaced by a revolving drum driven

through worm gearing by an electric motor. In order to reduce friction, smoked paper and a fine point on the indicator were used instead of the usual pencil. A facsimile of a diagram so obtained is shown in fig. 1, from

FIG. 1.—Record No. 19.



0.76 of original size. Scale of reproduction, 1 cm. = 4.7 lbs. per sq. in.

which it will be seen that there is slight oscillation due to the inertia. In the results recorded below a correction has been applied for these oscillations, a smooth curve being drawn in each case, but the maximum pressure is uncertain, perhaps by as much as 1 lb. per square inch. Six diagrams were also taken with the optical indicator of the piston and spring type which I designed some years ago for gas-engine work. Two diagrams given by this indicator are reproduced in fig. 2.* This diagram shows no

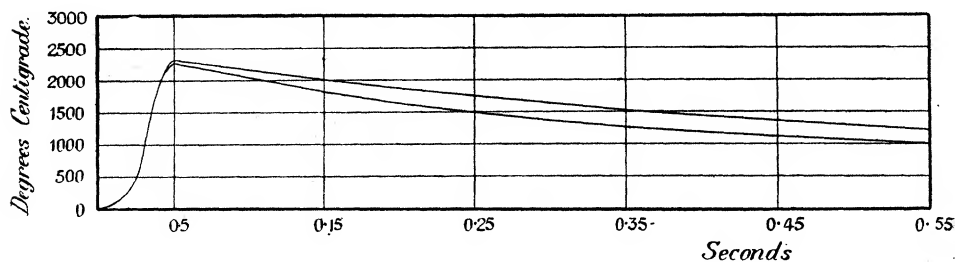


FIG. 2.

oscillation, and is probably in every respect more accurate than that given by the pencil instrument. It may be observed, however, that the errors of the latter instrument would not affect comparisons of different explosions taken under the same circumstances, except perhaps as regards maximum pressure.

In order to show the degree of accuracy reached it has been thought desirable to give all the results of the 27 satisfactory records which were obtained. Particulars of the procedure adopted in polishing are also given

* These diagrams, as also figs. 4 and 7, are exact tracings from photographic enlargements of the originals, the tracing being subsequently reduced in reproduction for printing.

Table I.

Record No.	Pressure, lbs. per square inch.					Polishing.
	Maximum pressure.	Times after ignition, secs.				
		0·15	0·25	0·35	0·45	
Pencil Indicator.						
1	111·9	96·6	86·2	76·5	—	First record taken in this vessel; polished with dry rouge.
2	109·0	95·0	82·7	74·2	—	Hand-polished with wash-leather.
3	107·8	85·5	68·3	58·0	50·5	Blackened.
4	109·0	—	72·5	—	—	Hand-polishing after blackening for (3).
5	107·6	—	72·4	—	—	Hand-polished.
6	105·9	83·3	68·2	57·5	49·9	Blackened.
7	109·5	97·0	84·2	—	—	Polished with motor-driven buff and dry rouge.
8	110·5	93·8	80·1	68·5	—	Hand-polished with wash-leather.
9	110·0	84·2	67·5	56·4	49·4	Blackened.
10	110·0	93·1	79·4	69·0	—	Polished with motor-driven buff and dry rouge.
11	110·0	92·6	79·0	69·5	—	Hand-polished.
12	111·7	87·0	71·9	61·0	53·5	Blackened.
13	110·4	87·0	70·8	60·1	52·5	„
14	111·0	98·6	88·4	79·6	71·0	Polished with motor-driven buff and rouge mixed with methylated spirits, re-washed with methylated spirits and hand-polished.
15	110·0	93·3	81·2	70·0	—	Hand-polished.
16	110·6	87·3	70·8	60·4	52·3	Blackened.
17	108·1	86·2	70·4	59·4	51·3	„
18	112·9	98·4	86·3	76·3	67·2	Polished as in (14).
19	112·0	95·1	81·1	—	—	Ditto, re-washing with methylated spirits omitted.
20	111·4	98·4	86·2	75·5	67·2	Polished as in (14).
21	110·2	86·3	71·1	60·3	53·0	Blackened.
Optical Indicator.						
I	114·0	98·7	84·2	73·5	64·9	Highly polished motor-driven buff and rouge, washed with methylated spirits and again polished.
II	114·0	98·7	84·2	73·5	65·4	Ditto.
III	110·8	89·2	73·1	61·3	53·5	Blackened.
IV	114·9	99·0	85·4	73·5	64·9	Highly polished as in I and II.
V	111·6	89·5	73·9	62·1	53·8	Blackened.
VI	111·2	89·1	73·9	62·1	54·7	„

in each case, as it was found that this had a material effect upon the results. The trials are separated into groups, each group being taken from one lot

of mixture in the tank, as described above. The barometric pressure and temperature varied from one group to another, and in order to make the results comparable the pressures recorded have all been reduced to a standard barometer of 760 mm. and a standard temperature of 12° C., on the assumption that the absolute pressure is proportional to the barometric height and inversely proportional to the absolute temperature of the mixture before explosion. In comparing the results of one day with another day it should, however, be remembered that the calorific value and composition of the gas vary slightly from day to day.

Looking first at the records of the explosions in which the walls were blackened, it will be seen that the two cooling curves from the same mixture agree at all points within 1 lb. per square inch. With the optical indicator (V and VI) the agreement is closer, and here it extends also to the maximum pressure. On account of oscillation the pencil indicator is not so reliable at maximum pressure. The results may be summarised as follows:—

Table II.—Blackened Walls.

	Maximum pressure.			0·25 sec.		
	Min.	Max.	Mean.	Min.	Max.	Mean.
Pencil (8 cards).....	105·9	111·7	109·3	68·2	71·9	70·0
Optical (3 cards)	110·8	111·6	111·2	73·1	73·9	73·6

The optical indicator reads appreciably higher than the pencil instrument. This may be partly due to a change in calorific value, but it is probable that there is also some difference between the instruments. Both were calibrated with dead weights.

The “polished” records do not show such good agreement, and it is at once apparent that the procedure followed in polishing is important, differences hardly apparent to the eye greatly affecting the rate of cooling. The 13 pencil records with polished walls show at 0·25 second pressures ranging from 72·4 to 88·4 lbs. per square inch, a range of 16 lbs. Explosions of identical mixtures give cooling curves which differ at this period by 5 or 6 lbs. per square inch. This uncertainty disappeared largely but not entirely after record 14, when the practice was adopted of washing the surface with methylated spirits so as to remove all traces of the shellac used in the previous blackening. By combining this washing with the use of a motor-driven buff more consistent results were obtained.

In what follows reference will only be made to those "polished" records in which this procedure was followed, namely, Nos. 14, 18, 20, 21, I, II, and IV. The results of these experiments agree moderately well, but it is evident that there are still differences in the walls which substantially affect the rate of cooling, though quite inappreciable to the eye.

(a) *Maximum Pressure.*—The maximum pressure reached with the polished walls is in every case higher than that reached with the blackened walls. The difference shown by the pencil indicator is in one group (14, 16, 17) 1.7 and in the other group (18, 20, 21) 1.9 lb. per square inch, the mean being 1.8; while the differences shown by the optical indicator are respectively 3.2 and 3.5 lbs. per square inch, the mean being 3.3. Taking the optical indicator as probably the more accurate, it follows that the maximum temperature reached with a polished lining is approximately 70° higher than that reached with the blackened lining. In considering this result it is to be remembered that the volumetric heat of the products of combustion is probably about 50 per cent. greater at this temperature than is the mean volumetric heat between 100° C. and 2000° C., so that the 3 per cent. difference in maximum temperature may represent something like 5 per cent. difference in total thermal energy. It is probable, however, that this 5 per cent. is not wholly represented by a difference in the heat which has been lost to the walls, but that it is partly due to incompleteness of combustion. At the moment of maximum pressure the rate of transformation of chemical into thermal energy just balances the rate of loss of heat to the walls. This heat loss being less when the walls are polished, the percentage of uncombined gas will also be less, since the rate of transformation of energy diminishes with the amount remaining to be transformed. Any effect of the reflecting state of the walls on the rate of combustion or on the ultimate state of equilibrium would, of course, invalidate this argument; such an effect is not impossible, but I have not yet discovered any evidence of it.*

(b) *Rate of Cooling.*—That the gas cools more slowly when the lining is reflecting is at once obvious from Table I or from fig. 2, which shows records I and III, obtained with the optical indicator from the explosion of

* Some recent experiments by Mr. W. T. David suggest that the state of equilibrium is not independent of the walls. He finds that the gas radiates more strongly at a given temperature when the walls are polished. If this be so, it must mean that the energy of the molecular vibrations is a greater proportion of the whole when the walls are polished than when they are black, and, consequently, that the energy of a gas enclosed in polished walls is greater than in black walls, though the temperatures (as inferred from the pressures) are the same. In other words, the apparent specific heat of a gas varies with the vessel in which it is contained. It cannot be said that this conclusion has yet been completely established, but it suggests some interesting possibilities.

the same mixture, superposed. The following table shows the time (from the moment of ignition) taken by the gas to cool to 1700°C . and 1200°C . respectively with different surfaces. Since the heat lost by the products of explosion in cooling to a given temperature must be very nearly the same whatever the state of the walls, the times are inversely proportional to the mean rate of cooling. This ratio is shown in each case, the rate of cooling with the black walls being taken as the unit.

Table III.

Record No.	1700°C .			1200°C .		
	Black.	Polished.	Ratio.	Black.	Polished.	Ratio.
14, 16, 17	0·178	0·320	0·56	0·297	0·567	0·52
18, 20, 21	0·177	0·289	0·61	0·302	0·473	0·64
I, II, III	0·193	0·269	0·72	0·320	0·455	0·70
IV, V, VI	0·196	0·277	0·71	0·327	0·450	0·73

It will be seen that the rate of loss of heat to the polished surface varies in different observations from rather over half to about three-quarters of the loss to black walls. The differences between one experiment and another cannot be ascribed in any large measure either to errors of observation or to the indicators. Indicator errors would affect both records equally and would not affect the ratios of times. It seems quite certain that in the optical records, which were taken together after all the others, the surface was not so good. Further there seems to be no reason to doubt that in explosion 14 the rate of cooling with the polished surface was not much more than half of that with the blackened walls. The tangents to the two cooling curves at corresponding points (that is points for which the temperatures are the same) tend to become parallel as the temperature falls. The slopes of these tangents are the ratio of the rates of heat-loss, which therefore tend to equality as the gas cools.

Comparisons similar to the above with a tin-foil lining first bright and then black showed that the ratio of rates of cooling down to 1200°C . was about 0·87. If the difference between this ratio and unity be taken as a measure of the radiation reflected it will be seen that tin-foil reflects for this purpose less than half as well as silver. It is not surprising, therefore, that no difference in maximum pressure could be detected with the tin-foil lining, using a pencil indicator.

Bolometric Measurements.

Having obtained the above results, it was decided to make bolometric determinations of the actual heat-loss to the walls and of the radiation. For this purpose a recording bolometer was devised, consisting of a silver or platinum strip whose resistance could be recorded on a revolving drum at the same time as the pressure developed by the explosion. The method used for recording the temperature of the strip was the same as that which I have described in a previous paper.* Briefly, it consists in passing through the strip a constant continuous current sufficient to produce some difference of potential at its terminals, balancing this difference by means of a source of

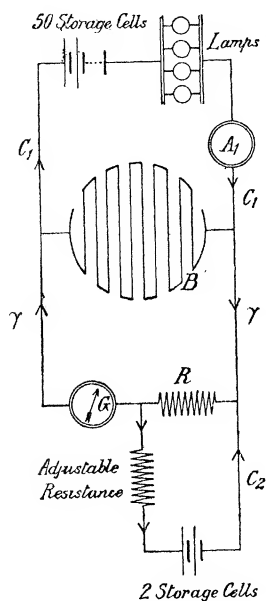


FIG. 3.

constant E.M.F., and recording by a reflecting galvanometer the increment of E.M.F. which arises when the strip is heated by the explosion. The deflection of the galvanometer is proportional to the increase in E.M.F., which again is proportional to the increase of resistance of the strip, and therefore to its rise of temperature. The connections are shown in fig. 3. The current C_1 passing through the bolometer B is taken from a number of storage cells working through a resistance high enough to ensure that the small variation of resistance in the bolometer during the explosion shall have no appreciable effect upon it. An ammeter A_1 is included in this part of the circuit, and the current is adjusted to a definite value before the experiment. The terminals of the bolometer are also connected to the recording galvanometer G through a resistance R , in which a current C_2 is maintained by means of storage cells in such a direction and of such amount

that the E.M.F. at the terminals of the bolometer when cold is approximately balanced. The resistances are such that C_2 does not appreciably vary when the bolometer is warmed. When the bolometer is heated the difference of potential between its terminals rises in proportion to the rise of temperature, while the balancing difference between the terminals of resistance R remains the same except for the small change in the current flowing in it consequent on the diversion of some part of the current C_1 from the bolometer to the galvanometer circuit. This change of current in R and in the bolometer is small, but as it is recorded on the galvanometer it can be allowed for if necessary.

* 'Roy. Soc. Proc.,' A, vol. 79, p. 138.

The recording galvanometer used in these experiments was of the ballistic suspended-coil type. The coil was of the standard pattern made by Messrs. R. W. Paul, but the usual suspension, which would give a period of about 4 or 5 seconds, was replaced by a much stiffer suspension, giving a period of about $1/25$ second; and for the usual permanent magnet was substituted an electro-magnet magnetised nearly to saturation, which gave a strong and fairly constant field, whose amount could be accurately adjusted to a definite value by a comparatively rough adjustment of the magnetising current. The resistance of the galvanometer was about 3.5 ohms, and its deflection was recorded photographically on the same revolving drum as that on which the pressures were recorded by the optical indicator.

It will be obvious that with the above arrangement the deflection of the galvanometer is nearly proportional to the increase of resistance of the bolometer strip; and this is so, even though exact balance is not obtained before the explosion. In order to get the relation between these two quantities, the current C_2 was reduced to zero* when the bolometer strip was cold, and the ratio was found between the galvanometer deflection under these conditions and the current in the bolometer strip, which latter was, of course, for this purpose reduced to a fraction of the value employed when taking explosion record. If c be the current under these circumstances corresponding to any deflection of the galvanometer, then, when there is a current C_1 shown on the ammeter A_1 , the proportion of increase in the bolometer resistance corresponding to the same deflection of the galvanometer is $\frac{c}{C_1 - \gamma}$, where γ is the current in the galvanometer.

Since the rise of temperature is directly deduced from the proportion by which the resistance rises, it will be seen that the calibration of the bolometer, that is, the reduction of galvanometer deflection to temperature increase, requires only an accurate knowledge of the ratio of the currents.

* Strictly speaking, this should be done by reducing the E.M.F. in the circuit C_2 to zero (short-circuiting the battery) and not by means of the adjustable resistance; and similarly the reduction of the current in circuit C_1 should be effected by a reduction in the E.M.F. of the battery. The resistances in the circuit being then all the same in calibration and in use, the relation between galvanometer deflection and change of resistance is given accurately in the manner described, being independent of the small changes in C_1 and C_2 consequent on the disturbance of the circuit by the increase of the bolometer resistance. In practice it is simpler to make the resistances in circuits C_1 and C_2 so large that they can be treated as infinite, and to use them for adjustment of current; but it must not be forgotten that any variation in either of these currents has the same effect as an equal percentage variation of the bolometer resistance. If, for example, it be desired to measure a rise of temperature of 40° C. correct to 1 per cent., the rise of resistance amounts to perhaps 15 per cent., and consequently C_1 or C_2 must be constant to within 1 part in 600.

c and C_1 , together with a rough knowledge of the galvanometer current γ , provided the latter is small compared with C_1 . In the experiments under consideration, γ never exceeded about 1 per cent. of C_1 , and could be neglected altogether.

(1) *Polished and Blackened Silver*.—The first bolometer used consisted of a plate of chemically pure silver, $1/5$ mm. thick, cut up so as to make a continuous strip having a resistance of 0.065 ohm at 14° C. The weight of the silver per square centimetre was 0.210 gramme, and it was mounted on a backing of linoleum $\frac{1}{4}$ inch thick, which was fixed on to the flat end-cover of the explosion vessel, a little above the centre. The temperature coefficient of the resistance of the silver was measured, and found to be 0.0040; its specific heat was assumed to be 0.056. The silver strip was fixed to the linoleum by means of shellac varnish and a few pins. Comparative records were taken with this bolometer first polished as highly as possible, and then blackened over, sometimes with the same blackening mixture as was used in the experiments described above, and sometimes with camphor smoke. The layer of black on the silver slightly increases its thermal capacity. The layer weighed something under 1 milligramme per square centimetre, equivalent to perhaps 0.2 milligramme of water, which is less than 2 per cent. of the heat capacity of the silver. This small addition is neglected in what follows, the heat capacity of the bolometer being supposed the same whether blackened or not. A considerable number of records were taken with the bolometer in these two states. The rest of the surface was blackened in all cases.

Tracings of two records are shown superposed in fig. 4; the pressure records in these two cases were identical. It will be seen that the galvanometer is thrown in slight oscillation by the sudden increase in heating

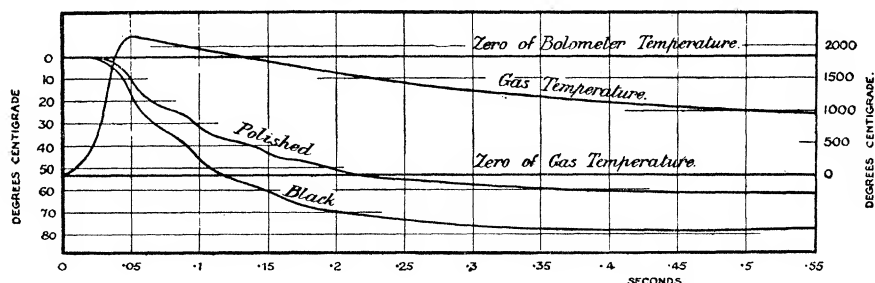


FIG. 4.

when the flame strikes the bolometer. The temperatures of the silver shown in these records after smoothing the oscillations are given in the following table, their ratios being shown in the fifth column:—

Table IV.

Time (from ignition).	Gas temperature.	Bolometer temperatures.		Ratios of temperatures.	Ratios of heat absorbed.
		Black.	Polished.		
0·05	2150	15·9	12·0	0·755	0·755
0·10	1940	45·8	31·9	0·695	0·70
0·15	1750	61·0	44·1	0·725	0·72
0·20	1590	70·0	51·7	0·74	0·73
0·30	1350	76·8	59·0	0·77	0·75
0·50	1030	78·7	62·5	0·795	0·77

In the course of being heated by the flame the silver loses a considerable quantity of heat to the backing with which it is in contact. The percentage of heat so lost depends upon the thermal conductivity and the thermal capacity of the backing, and on the manner in which the temperature of the silver rises. If the two curves for polished and blackened silver were precisely similar, differing only in respect of the scale of temperature, the proportion of heat lost at corresponding times would also be the same for both, and the quantity of heat absorbed would be proportional to the temperature. The curves are not quite of the same shape, and the small correction applicable on this account has been calculated and is allowed for in the last column. The figures there given represent, probably within 5 per cent., the proportion in which the black and polished silver surfaces absorb heat when exposed to gas temperatures varying in the manner shown by the above record. It appears that the mean rate of absorption during the first quarter of a second by the polished surface is 0·74 of the absorption by the blackened surface. The records of pressure obtained with polished and blackened walls, to which reference is made in section (b) above, showed that the mean rate of cooling in a polished vessel during the first quarter of a second was in different experiments from 0·56 to 0·71 of the rate observed when the walls are blackened. The agreement is as good as can be expected, having regard to the great effect of small variations in the state of polish. The bolometer also shows that approximation of the rates of cooling in the two cases as the temperature falls which appeared in the pressure records. The difference in heat absorption represents no doubt the greater part of the radiant heat emitted by the gas in the time, but it does not represent the whole of it. For the black surface is not perfectly absorbent, nor is the polished surface perfectly reflecting. Thus it is quite certain that of the heat given by the gas to the walls of a blackened enclosure during the first quarter-second after maximum pressure, at least 30 per cent. is radiant heat, and the proportion is probably a good deal higher.

The absolute determination of the quantity of heat-loss represented by the rise of temperature of the bolometer strip cannot be effected very accurately, owing to the large proportion of heat lost to the backing. In order to estimate this proportion, the backing may be considered as an infinite solid, the temperature θ of whose plane face is at each instant that of the silver, and is therefore known in terms of the time from the record. Let k and c be the thermal conductivity and thermal capacity per unit of volume respectively of the backing. Then it is easy to show that the total heat which has passed into the backing at time T (reckoned from some moment before the silver began to warm up (say the moment of ignition) is

$$2 \sqrt{\frac{kcT}{\pi}} \int_0^T \frac{d\theta}{dt} \sqrt{1 - \frac{t}{T}} \cdot dt.$$

The proportion which the total heat which has passed into the backing bears to that remaining in the silver ($C\theta_T$) is then

$$\frac{2}{C} \sqrt{\frac{kcT}{\pi}} \cdot \frac{1}{\theta_T} \int_0^T \frac{d\theta}{dt} \sqrt{1 - \frac{t}{T}} \cdot dt.$$

The fraction $\frac{1}{\theta_T} \int_0^T \frac{d\theta}{dt} \sqrt{1 - \frac{t}{T}} \cdot dt$ is easily obtained graphically for various values of T from the graph of θ , and depends only on the shape of that graph, being independent of the scale to which it is drawn. To complete the calculation of the proportion of heat lost, it is only necessary to find or estimate the quantity $\frac{2}{C} \sqrt{\frac{kc}{\pi}}$. This might be done by direct measure-

ment of the thermal conductivity and thermal capacity of the backing. The fact that the silver does not cover the whole surface, and that there is a layer of shellac of varying thickness between it and the linoleum, however, introduces a good deal of uncertainty. A more accurate method is to compute the total energy in the gas from its temperature at some time when it has cooled so far that its specific heat may be considered known, and to calculate the total loss of heat at that instant by deducting the energy from the heat developed in the combustion. Comparing this heat-loss with

the heat then accounted for in the silver, a value of $\frac{2}{C} \sqrt{\frac{kc}{\pi}}$ may be found, which value can be used for computing heat-loss at earlier periods when, from want of accurate knowledge of the internal energy of the gas, it cannot be determined directly. The thermal conductivity and capacity of the backing determined in this way will be effective values of these quantities, in which the various factors of incomplete covering, etc., are taken into account.

Applying this method in the present instance, it has been found that 0.5 second after firing, when the temperature of the gas is 1000°C ., the total heat-loss to the walls (averaged over the whole surface) is 2.5 calories per square centimetre.* The temperature of the blackened silver is then 79°C ., equivalent to 0.93 calorie per square centimetre in the silver. The heat lost to the backing at this epoch is therefore $2.5 - 0.93 = 1.57$ calorie per square centimetre. It is here assumed that the heat absorbed by the bolometer is equal to the average absorption over the whole surface. When $T = 0.5$, we have, therefore,

$$\frac{2}{C} \sqrt{\frac{kcT}{\pi}} \cdot \int_0^T \frac{1}{\theta_T} \frac{d\theta}{dt} \sqrt{1 - \frac{t}{T}} \cdot dt = \frac{1.57}{0.93} = 1.69.$$

The value of the integral is obtained from the record of temperature (see fig. 4), and is found to be 0.895 when $T = 0.5$. It follows that

$$\frac{2}{C} \sqrt{\frac{kc}{\pi}} = 2.7.$$

A direct measurement of the thermal conductivity and thermal capacity of the linoleum, by methods which need not be described here, gave

$$k = 0.00032,$$

$$c = 0.62,$$

whence

$$\frac{2}{C} \sqrt{\frac{kc}{\pi}} = 1.35,$$

or only about half the value given by the other method.

Assuming that $\frac{2}{C} \sqrt{\frac{kc}{\pi}}$ is equal to 2.7, the following table shows the absolute quantities of heat absorbed by the blackened and polished surfaces per unit area at different times. The second column gives the temperatures reached by the two bolometers; the third, the corresponding heat quantities in the silver (calculated on the assumption that the specific heat of pure silver is 0.056); the fourth, the factor $\frac{2}{C} \sqrt{\frac{kcT}{\pi}} \cdot \frac{1}{\theta_T} \int_0^T \frac{d\theta}{dt} \sqrt{1 - \frac{t}{T}} \cdot dt$, which gives the proportion of heat lost to backing; and the fifth, the actual absorption after allowing for this loss. The sixth column is the difference in the heat absorption of the blackened and polished surfaces.

If the absorption by the bolometer is equal to the average over the whole surface of the vessel, the total heat lost to the walls of the blackened vessel at maximum pressure (0.95 second) is 1080 calories, or $6\frac{1}{2}$ per cent. of the whole heat of combustion. This agrees well with the results of experiments

* See Appendix.

Table V.

Time.	Temperatures ° C.			Heat in silver, calories per sq. cm.		Proportion lost to backing.		Total absorption.		Difference calories per sq. cm.
	Gas.	Silver.								
		B.	P.	B.	P.	B.	P.	B.	P.	
0·05	2150	15·9	12·0	0·188	0·142	0·30	0·30	0·245	0·185	0·06
0·10	1940	45·8	31·9	0·530	0·376	0·50	0·50	0·795	0·565	0·23
0·15	1750	61·0	44·1	0·720	0·520	0·70	0·69	1·22	0·88	0·34
0·20	1590	70·0	51·7	0·826	0·610	0·90	0·88	1·57	1·15	0·42
0·30	1350	76·8	59·0	0·906	0·696	1·22	1·18	2·01	1·52	0·49
0·50	1030	78·7	62·5	0·929	0·737	1·70	1·63	2·51	1·94	0·57

in which the resistance of a copper strip completely lining the vessel was recorded.* These experiments showed a total loss of 1200 calories, or 7·5 per cent., at the moment of maximum pressure after the explosion of a 15-per-cent. mixture. The difference between the absorption of the blackened and polished surfaces at this moment would amount to 260 calories for the whole vessel, or about 2 per cent. of the heat of combustion. As already stated, the observed difference in maximum temperature probably corresponds to 5 per cent. in the thermal energy. The balance, which amounts to 2 or 3 per cent., represents a difference in completeness of combustion, in favour of the polished walls.

(2) *Bolometer behind Fluorite Screen.*—A direct measurement of the radiation was obtained by a recording bolometer placed outside the vessel behind a fluorite window. This instrument, which was designed by Mr. W. T. David, is shown in figs. 5 and 6. It consists of a platinum strip (fig. 5) mounted on the end of a hollow wooden cylinder. The strip weighed 0·25 gramme per square centimetre and had a thermal capacity of 0·008 gramme of water per sq. cm. (specific heat assumed to be 0·032).

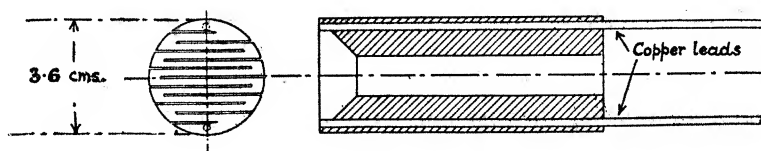


FIG. 5.

The resistance was at first 0·15 ohm, but was reduced in later experiments by short-circuiting two of the coils to about 0·115 ohm (room temperature). The temperature co-efficient was measured and found to be 0·0036. The

* Full details of the method are given in 'Roy. Soc. Proc.,' A, vol. 79, p. 139.

connections of the bolometer were the same as in the experiments last described (blackened and polished silver—see fig. 3). The bolometer, which was blackened with camphor smoke, was pushed into a gun-metal tube screwed into a boss on the end-cover of the vessel, which carried at its inner end the plate of fluorite (fig. 6).

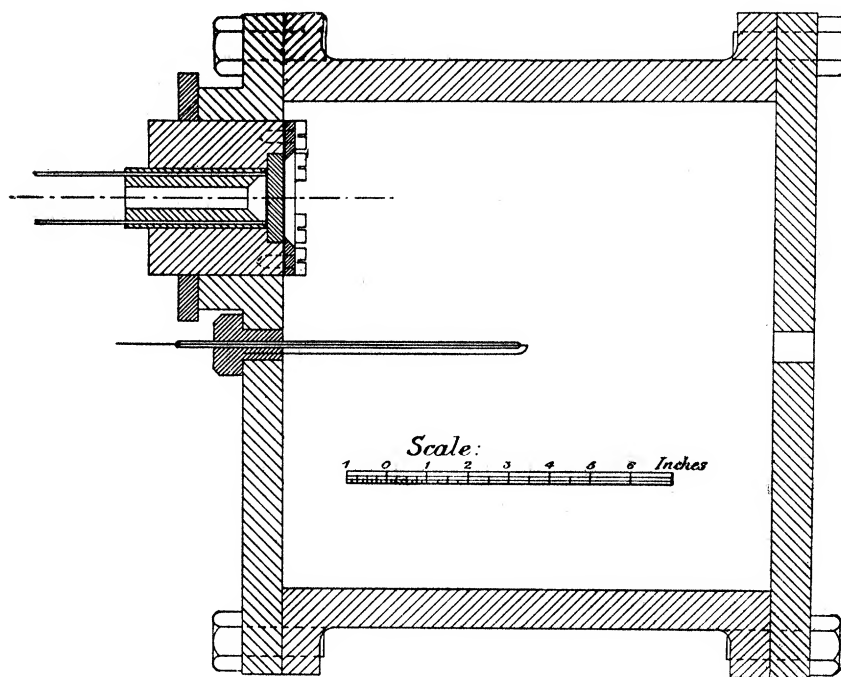


FIG. 6.

The fluorite was $\frac{1}{4}$ -inch thick, and the clear opening $1\frac{1}{2}$ inch diameter. The interior of the vessel was blackened.

One record taken under these conditions during the explosion of 15-per-cent. mixture is reproduced in fig. 7. The figure is an exact tracing from an enlargement of the original. It is noteworthy that there is no oscillation of

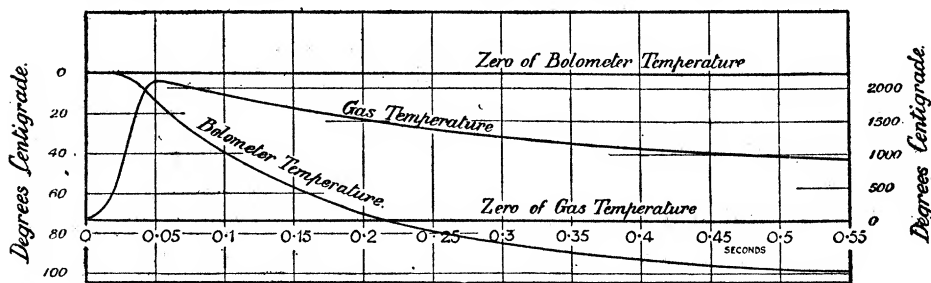


FIG. 7.

the galvanometer, doubtless because there is no sudden heating such as occurs when the flame touches a surface in contact with the gas. The following table shows the results of this record:—

Table VI.

Time from ignition.	Temperature ° C.		Heat in platinum, calories per sq. cm.	Loss.	Total absorbed, calories per sq. cm.	Percentage of heat of combustion.
	Gas.	Platinum.				
0·05	2090	13·6	0·11		0·11	3
0·1	1870	39·6	0·315		0·315	8·5
0·15	1690	57·4	0·46		0·46	12·5
0·2	1510	70·3	0·57		0·57	15·5
0·3	1290	84·2	0·675	0·025	0·70	19
0·4	1110	91·7	0·735	0·035	0·77	21
0·5	980	96·4	0·770	0·05	0·82	22

The loss of heat from the platinum by conduction and radiation (shown in the fifth column) was determined by calculation from the rate of fall of temperature in the later stages of cooling, when no radiation was being received. The percentages in the last column are calculated on the assumption that radiant heat is absorbed by every part of the blackened walls at the same rate as by the bolometer, no allowance being made for absorption in the fluorite or reflection from the bolometer. Probably about 10 per cent. should be added on this account to get the true amount of radiation.

The amount of radiation shown in this experiment is from 40 to 50 per cent. in excess of that given by comparison of the blackened and polished silver bolometer inside the vessel, at corresponding times. The uncertainty attaching to the latter observations, partly because they are difference measurements, and partly because of the very large corrections for loss to the backing, will not have escaped observation. I think, however, that the discrepancy is too great to be accounted for in this way, and that the difference between the absorption by the blackened and polished silver surfaces is really a good deal less than the whole of amount of radiation. Mr. W. T. David has suggested that a film of water may perhaps be formed on the polished surface at an early stage of the cooling and impair its reflecting qualities. About 5 grammes of water are produced in the explosion, and practically the whole of this ultimately condenses on the walls, covering them to an average depth of 1/100th of a millimetre all over, thus destroying in large measure their reflecting power. It is probable that the formation of this layer commences almost as soon as the flame touches the metal, and that a much thinner layer

would be adequate to absorb a considerable fraction of the radiation falling upon it. The fluorite plate, on the other hand, must almost instantly become too hot on the surface to admit of the deposit of moisture. It is possible that the rate of formation of this film depends on the exact state of the metal surface, and that we have here the explanation of the great effect of apparently inappreciable differences in polish on the rate of cooling.

It was found that if a plate of glass was substituted for the fluorite, the heat received by the bolometer was reduced to about one-third; and that if the platinum were polished the heat received was only about 20 per cent. of that recorded with a blackened surface. The latter proportion agrees with the figure given by Hagen and Rubens for the reflecting power of polished platinum.

The experimental work described in this paper has been carried out by Mr. W. T. David, advanced student at the Engineering Laboratory, to whom I am much indebted for the ability and zeal with which he has prosecuted the research and for many suggestions of value. He is engaged upon experiments with the recording bolometer similar to those last described, by which it is hoped to determine the nature and origin of the radiation, and its dependence on temperature and density. The work of R. von Helmholtz* and of Julius† proves that the radiation from a non-luminous flame (*e.g.* a Bunsen flame) burning at atmospheric pressure consists mainly of two bands, of wave-lengths $4.6\ \mu$ and $2.8\ \mu$, which come from the carbonic acid and steam respectively. It is probable that the radiation in a closed-vessel explosion is of substantially the same quality, and Mr. David's work, so far as it has gone, confirms this view.‡

APPENDIX.—*Calculation of Heat-Loss from Pressure Record.*

At 0.5 second from the time of ignition the mean temperature of the gas calculated from the pressure is nearly 1000°C . The energy is shown in the following table:—

* 'Die Licht- und Wärmestrahlung verbrennender Gase,' Berlin, 1890.

† 'Die Licht- und Wärmestrahlung verbrannter Gase,' Berlin, 1890.

‡ It has been suggested that possibly some of the radiation comes from the walls of the vessel, which are heated by the explosion. From consideration of the rate of flow of heat per sq. cm., however, it can be shown that the surface temperature of the metal can never exceed about 40°C ., which is of course quite inadequate to give any appreciable radiation. Further, Mr. David has found that if a patch of the wall opposite the bolometer be highly polished, the radiation received is *increased*. The fluorite plate will be heated to a fairly high temperature at the inner surface, but the radiation emitted by this surface will be absorbed in the fluorite and none of it will reach the bolometer. No appreciable heating of the outer surface can occur during the measurement of the radiation.

Table VII.

Gas.	Volume (gramme-molecule).	Energy 1000° to 100°.
CO ₂	0·09	$9000 \times 0·09 = 810$
H	0·21	$6500 \times 0·21 = 1370$
N	0·70	$5000 \times 0·70 = 3500$
Total.....	1·00	5680

The first factor in the energy of each constituent is the quantity of heat (in calories) evolved by that constituent per gramme-molecule (taken to be 22·25 standard litres in each case) in cooling at constant volume from 1000° to 100° C. These energies are calculated from the results of Holborn and Henning for the specific heat of these gases, but a correction of 5 per cent. has been added in each case because there is reason to suppose that Holborn and Henning's values are too low. The figures are uncertain to the extent of about 5 per cent. The quantity of gas present is 20·3 litres under standard conditions, or 0·905 gramme-molecule (volume of vessel 22·3 litres, pressure before explosion 763 mm., temperature before explosion 16° C., contraction 4 per cent.). Hence the total heat present in the gas (reckoning from 100° C.) at 0·5 second is 5200 calories. The heat evolved by burning the coal gas, taking a calorific value of 115,000 calories per gramme-molecule (580 British thermal units per standard cubic foot, lower value), is

$$0·15 \times 115,000 \times 0·945 = 16,300 \text{ calories,}$$

since the volume before combustion is 4 per cent. greater than after. Hence at this time the total heat which has passed into the walls is $16,300 - 5,200 = 11,100$ calories. The total surface of the vessel is 4380 square centimetres, so that the average loss per square centimetre is about 2·5 calories.
